

Oxide Dispersion Strengthened Alloys

Prepared for the NASA Research Advisory Committee on Materials by NICHOLAS J. GRANT, Massachusetts Institute of Technology; HOWARD J. SIEGEL, McDonnell Company; and ROBERT W. HALL, Lewis Research Center, NASA



Scientific and Technical Information Division

OFFICE OF TECHNOLOGY UTILIZATION

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C.

1967

Members

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
RESEARCH ADVISORY COMMITTEE ON MATERIALS

LOUIS R. MCCREIGHT, *Chairman*
General Electric Co.
Philadelphia, Pa.

DAVID C. GOLDBERG
Westinghouse Electric Corp.
Pittsburgh, Pa.

ALAN V. LEVY
Aerojet-General Corp.
Sacramento, Calif.

FRED D. ROSI
Radio Corp. of America
Princeton, N.J.

NICHOLAS J. GRANT
Massachusetts Institute of Technology
Cambridge, Mass.

HOWARD J. SIEGEL
McDonnell Company
St. Louis, Mo.

WOLFGANG H. STEURER
General Dynamics Corp.
Fort Worth, Tex.

MILTON C. SHAW
Carnegie Institute of Technology
Pittsburgh, Pa.

THOMAS G. FOX
Mellon Institute
Pittsburgh, Pa.

WILLIAM A. TILLER
Stanford University
Stanford, Calif.

ELDON E. MATHAUSER
NASA Langley Research Center
Hampton, Va.

JAMES D. CHILDRESS
NASA Electronics Research Center
Cambridge, Mass.

PHILIP GOODWIN
U.S. Navy Department
Washington, D.C.

NATHAN E. PROMISEL
Executive Director
Materials Advisory Board
NAS-NRC, Washington, D.C.

LEE R. STANDIFER, Col., USAF
Wright-Patterson AFB
Dayton, Ohio

JULES M. SIMMONS
U.S. Atomic Energy Commission
Washington, D.C.

HENRY E. FRANKEL
NASA Goddard Space Flight Center
Greenbelt, Md.

HOWARD E. MARTENS
NASA Jet Propulsion Laboratory
Pasadena, Calif.

CHARLES A. HERMACH
NASA Ames Research Center
Moffett Field, Calif.

ROBERT E. JOHNSON
NASA Manned Spacecraft Center
Houston, Tex.

WILLIAM R. LUCAS
NASA Marshall Space Flight Center
Huntsville, Ala.

ROBERT W. HALL
NASA Lewis Research Center
Cleveland, Ohio

JOSEPH MALTZ, *Executive Secretary*
NASA Headquarters
Washington, D.C.

For Sale by the Superintendent of Documents,
U.S. Government Printing Office, Washington, D.C. 20402

Price 15 cents.

Library of Congress Catalog Card Number 67-60087

Foreword

The NASA Research Advisory Committee on Materials has, as part of its charter, the responsibility of identifying promising new materials concepts of significance to advanced aerospace systems, suggesting the course of research to advance the level of understanding of such concepts, and stimulating their development toward full utilization.

At a meeting of the Committee in January 1966, the following question was raised:

Why have oxide dispersion strengthened alloys not achieved greater commercial success in view of the considerable lapse of time since the first awareness of the potential of metal-metal oxide materials and in view of the extensive work done on such systems in the meantime?

The question properly deserves an answer, since Sintered Aluminum Powder (SAP), which is generally considered the prototype of such alloys, was announced as far back as 1950.

A panel of the Committee was formed, accordingly, to consider this question. The members of the panel were Nicholas J. Grant, Massachusetts Institute of Technology, Chairman; Howard J. Siegel, McDonnell Company; and Robert W. Hall, Lewis Research Center, NASA. This report is the result of the deliberations of that panel. Observations herein are based primarily on material available through the open literature. A number of industrial developments were known to be underway. However, these were not documented well enough to permit accurate reporting and dating. Some of these developments have emerged recently or are now emerging, and are important contributions to the development and commercialization of oxide dispersed alloys.

Although mainly the work of Professor Grant, this study represents the opinion of all panel members as well as of others solicited for views in the course of the inquiry. Their individual

comments are given in the appendix to this report. On the recommendation of the Committee, it is being published so that it may be available for use by all who are interested in the subject.

JOSEPH MALTZ
Executive Secretary
NASA Research Advisory
Committee on Materials

Contents

SUMMARY	1
INTRODUCTION	2
EARLY HISTORY	2
PROGRESS	4
CURRENT SITUATION	5
DISCUSSION AND RECOMMENDATIONS	10
APPENDIX	13
REFERENCES	24

Summary

The observations and conclusions resulting from the study of oxide dispersion strengthened alloys may be summarized as follows:

- Oxide dispersed alloys, as serious contenders for use as high temperature materials, were looked at almost casually until about 3 or 4 years ago. They are, therefore, at an early point in their development and considerable additional work must be undertaken to test their potential.
- Until recently effort has been concentrated on systems with unalloyed matrices. Work with alloyed matrices is only just beginning. In particular, matrices utilizing oxidation resistant systems will require considerable additional effort. The stability of the refractory oxide in such alloys is largely unknown and must be determined.
- The mechanism of strengthening must be clearly established. Deformation and fracture studies must be pursued simultaneously.
- Dispersoids other than oxides should be examined.
- At least 5 years of increased support must be programmed. Such support must come at a considerably higher level than that which prevails.
- Important alloys of commercial stature can confidently be expected to result from such an expanded program.

Introduction

The announcement of SAP (Al-Al₂O₃ alloy, Sintered Aluminum Powder) about 1950 (ref. 1) was an important event to materials science. This new alloy was enormously more resistant to degradation of structure and mechanical strength at elevated temperatures than were conventional aluminum alloys. Nevertheless it was simple in composition and was, in fact, made from materials which were potentially plentiful and inexpensive. Furthermore, there was a strong possibility that the techniques for its manufacture could be applied, with some modifications, to other alloy systems.

SAP also offered an exciting challenge to the theoretician. Its properties were not really explainable by any of the prevailing theories of alloy strengthening which meant that a study of SAP might light the way to a new understanding of two-phase metal systems, generally.

Today this promise is only partially realized. SAP itself has been used in a few instances for military and commercial hardware, but there is a feeling that these are relatively trivial. Many other metal-metal oxide systems have been formulated and studied, yet only a few are even close to commercial use. The object of this report is to look into the reasons for this apparent discrepancy, to reexamine the prognosis for the oxide dispersion strengthened alloys, and to spell out the research which must be done to realize the hoped-for breakthrough.

Early History

The first announcement of SAP did not actually signal the origin of oxide dispersion strengthened alloys. There had been earlier indications that such a strengthening mechanism was available. These included the work on thoria stabilized tungsten wire (for incandescent lamps) and the relatively extensive work on oxide strengthened structures achieved by internal oxidation (refs. 2 and 3).

Publications reporting structures and some properties can therefore be dated from about 1940. Unfortunately, these early disclosures generated only a minor interest. It was nearly 1955–1956 (ref. 4), after their similarity to the research on SAP became obvious, before their potential was fully appreciated.

What SAP did do was to act as a powerful stimulus to seek other alloy systems which would be useful as constructional materials over a broad temperature range. However, even this stimulus required considerable time to mature. The net result is that serious work on other useful oxide dispersion strengthened alloys can only be said to have begun in the late 1950's.

Even the inventor, R. Irmann, and his coworkers could do little to explain the unusual high-temperature strength of SAP, especially in view of its relatively low properties at room temperature (refs. 1 and 5 to 7). The first efforts in this country, not surprisingly, were directed toward confirming and duplicating the European results in the aluminum–aluminum oxide system (ref. 8). At about the same time, Swiss material was sent to MIT for testing and evaluation in the hope of learning more regarding the mechanism of strengthening. A preliminary report of the results of this study (ref. 9) was followed a short time later by a considerably more detailed paper by Gregory and Grant (ref. 10). This was one of the first theoretical treatments of the possible mechanism of strengthening. It established the role of oxide particle size and interparticle spacing. There was some skepticism that the electron-micrographs it contained were representative of the structure of SAP, until the results were largely substantiated by the independent results of Lenel et al. (refs. 11 and 12).

Up to this point, SAP and the Alcoa experimental aluminum alloys were considered by many to be something of an oddity, incapable of being duplicated in other metal and alloy systems. A new and exciting materials development concept was involved, but the method of producing the materials was unique. The fact that aluminum presented an ideal situation wherein fine flakes carried along their own ultrathin oxide skins suggested that methods of incorporating oxides in other systems, on the same scale, were out of the question.

The first demonstration of the wider applicability of concepts learned from SAP alloys was made in 1956 and published a year later. Desired structures were successfully incorporated into copper,

a metal quite dissimilar from the ideally oxidizing metal aluminum (refs. 13 and 14). In point of fact, a somewhat earlier publication had reported enhanced high-temperature properties for oxide strengthened molybdenum but had gone largely unnoticed (ref. 15). Its confirmation of benefits from oxide dispersions incorporated by powder metallurgical techniques was actually an important addition to the field.

Thus, the birth of oxide dispersion strengthened alloys dates from the time of the tungsten-thoria W-ThO₂ alloys, but the utility of such alloys for general commercial use became evident only after 1956. The role of SAP was to provide an early stimulus. The real activity waited until the meaning of this stimulus could be appreciated.

Progress

Only a few isolated groups studied dispersion strengthened alloys during the period from 1956 to about 1960. To understand why these materials received so much less attention than they deserved, let us examine what there was to work with for the several years after 1956.

(1) There were no pure metals or alloys finer than about -325 mesh (-44 microns), and the quality was poor to fair, at best. Sherritt Gordon Mines, Ltd., was the sole source of a new class of 5-micron pure metals for a number of years; the powders were quite pure and did much to advance the state of the art. There was no other source of similar fine metal powders.

Fine alloy powders were expensive and of poor quality. They were highly oxidized and prone to flaking. In fact, it was well after 1960 that the first relatively high-grade alloy powders began to appear on the market in small experimental lots.

A number of developmental efforts to apply coarse impure powders almost destroyed the interest in metal-metal oxide alloys through adverse reports on properties.

(2) By comparison the availability of suitable dispersoids was a bright spot. Certain oxides were readily available as fine as 0.01 micron (100 Å). These were SiO₂ (0.01 micron) and Al₂O₃ (0.02 to 0.03 micron). A number of other oxides (e.g., ZrO, MgO) were available in the 0.05- to 0.2-micron range.

(3) Since structure parameters had to be established, work was logically done on the most simple, purest material available:

namely, pure metals. Copper and nickel, both available finally as 1- to 5-micron powders, were the prime matrix materials. Along with SAP and a minor amount of internal oxidation work, mechanical blending methods (refs. 16 and 17) were generally utilized to produce alloys to establish the role of:

- (a) particle size
- (b) particle shape
- (c) interparticle spacing
- (d) dispersoid solubility or insolubility considerations
- (e) stored energy, or alternatively, the mechanism of strengthening.

The first publication describing the strengthening of copper with SiO_2 and Al_2O_3 , utilizing coarse (-200 and -325 mesh) copper powders (refs. 13 and 14), did not appear until 1957. The same year, evidence was presented to suggest that stored energy of cold work was the mechanism of strengthening.

(4) Refinements in structure control came only in 1960 when internally oxidized copper alloys were shown to be as strong as SAP (ref. 18) and more efficient in their structure.

Moving on to 1960, the oxide dispersion strengthened alloy picture was as follows:

(1) There were no commercial sources of suitable, adequately pure, near micron alloy powders.

(2) There were no commercial processes on the horizon for high-grade, near micron alloy powder production, especially of the oxidation resistant types.

(3) Du Pont, Monsanto, Curtiss-Wright, and Sherritt Gordon were showing increasing activity in the metal-metal oxide field, all using different chemical methods to produce the alloys.

(4) The number of fundamental and applied engineering programs on metal-metal oxide systems was quite small.

(5) SAP was a production item but applications were few and of limited interest.

Current Situation

No effort will be made to summarize, other than in a limited way, the situation as it has evolved since about 1960.

(1) Du Pont has succeeded in producing a strong, highly stable alloy, TD-Nickel, by a closely controlled chemical process, operating on a pilot scale. Hot extrusion at a low extrusion ratio is

(2) Sherritt Gordon Mines, Ltd., has succeeded in producing by a unique and inexpensive chemical process DS-nickel equivalent in strength to TD-Ni. This organization is now investigating alloyed matrices, including oxidation resistant nickel-chromium alloys. The Sherritt Gordon process is primarily intended for high nickel alloys; it could conceivably be used for cobalt or iron base matrices, but this would call for new developments. Results at 1800° F and above with oxidation resistant alloys are similar to those achieved by Du Pont.

The data on TD-Ni and DS-Ni are documented in the literature and Defense Metals Information Center reports. The work on alloys is appearing currently as progress reports.

(3) Teledyne Materials Research Company (formerly New England Materials Laboratory) is able to report the following property data, based on work under industrial sponsorship, for alloyed metal-metal oxide systems, including oxidation resistant alloys:

(a) For stainless steel-ThO₂ alloys (unpublished): 0.2 percent yield strength at room temperature, 100 000 to 160 000 psi; ultimate tensile strength at room temperature, 120 000 to 180 000 psi; elongation at room temperature, 6.0 to 1.0 percent; stress for 100-hour life at 1500° F, 27 000 psi; stress for 1000-hour life at 1500° F, 22 000 psi; stress for 100-hour life at 1800° F, 6500 psi.

As shown in figure 1, the stainless steel-thoria alloy shows almost a tenfold increase over unmodified type 304 stainless steel in stress to rupture at 1500° F. When compared with L-605, a cobalt-base superalloy, it shows a modest advantage under conditions leading to rupture in short times and a greater advantage under long-time conditions. If the comparison is made with René 41, a highly alloyed nickel-base alloy, the data from long-time creep tests at 1500° F show this stainless-steel alloy to be stronger than René 41 for lifetimes greater than about 25 000 hours. This is a good measure of long-time stability, even at temperatures lower than those usually considered ideal for this class of alloy.

(b) For A5L, a matrix-strengthened SAP-type aluminum alloy containing 4.4 percent magnesium and 7 percent Al₂O₃ (discussed in paper entitled, "Solid Solution Strengthened SAP-Type Alloys" by A. S. Bufferd and N. J. Grant, to be published in *Metals Quarterly*, Am. Soc. for Metals), 0.2 percent yield strength, 56 000 psi; ultimate tensile strength, 64 000 psi; elongation, 3 percent, all at room temperature. The use of magnesium in solid solution

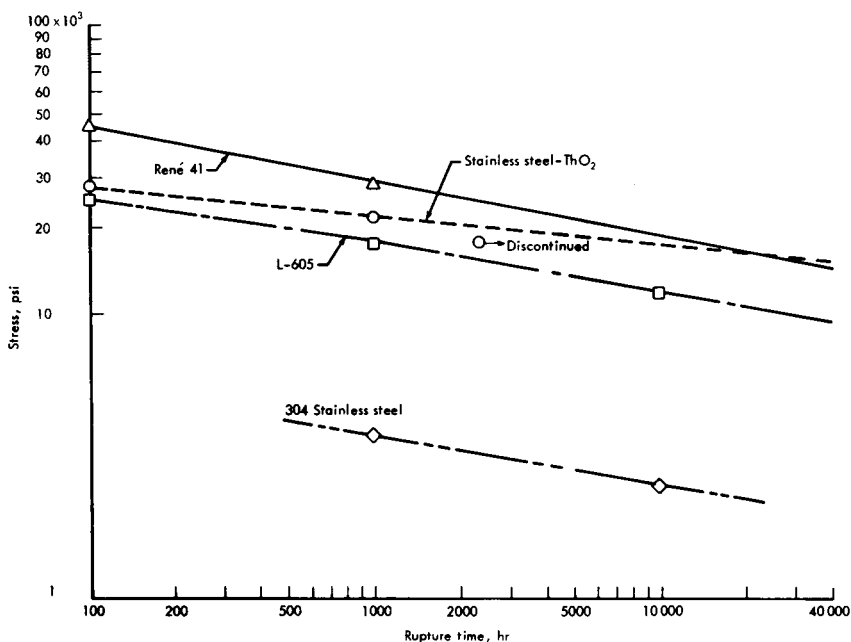


FIGURE 1.—Comparison of stress-rupture time for several materials at 1500° F.

has increased the room-temperature strength to a level which compares favorably with that of the precipitation hardened strong alloys and which is more than double that of regular 8 percent Al_2O_3 SAP, as shown in figure 2. This overcomes one of the major objections to the use of $\text{Al-Al}_2\text{O}_3$ alloys in aircraft structures and engine parts.

The A5L alloy maintains an advantage over 12 percent Al_2O_3 SAP in short-time strength up to 600° F. Beyond this temperature the two alloys remain equal.

In creep tests at 400° F, the times required to reach 0.1 percent total plastic strain may be compared as follows:

2024-T4	10 hours at 13 500 psi
14 percent Al_2O_3 SAP	100 hours at 13 000 psi
A5L.....	2000 hours at 13 300 psi and 1000 hours at 15 400 psi

(4) NASA has initiated a series of programs in an effort to develop improved processes and superior alloys. NASA itself pursues an active in-house program which has developed a number of important items of information. Two are:

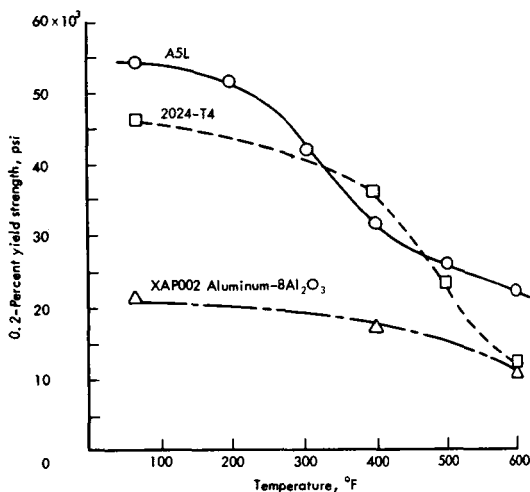


FIGURE 2.—Variation of yield strength with temperature.

(a) the role of alloy cleanliness on stability at the higher temperatures;

(b) the role of surfactants as grinding aids to help produce submicron metal and alloy powders.

(5) The United States Air Force is supporting work at a number of facilities to help scale-up alloy capability. Outstanding properties at 1800° F are reported for a Ni-Mo-ThO₂ alloy under such a program.

(6) Uses of SAP are increasing. While SAP is not a tonnage material, a number of uses for which it is uniquely suited have been found, notably a material for fuel tube containers for lower temperature nuclear reactors. Such applications are in common use both in Europe and the United States (refs. 20 and 21).

(7) In the U.S.S.R., from 1959 to 1962 (publication dates are later, ref. 22), starting from a position where no fine flake aluminum was available, SAP has been produced at oxide levels up to 20 volume percent, in compact sizes up to 1 ton, in bar diameters up to 8 inches, in tubes up to 8 inches outside diameter, in sheets up to 48 inches wide. Over 60 high-grade publications have emerged from this concentrated effort alone; the program was well balanced between fundamental and applied efforts. Welding and brazing were both carried out successfully; clad SAP was developed to simplify both welding and brazing; scrap SAP was utilized (ap-

parently) successfully; and a number of new applications were reported.

Properties reported at room temperature for unalloyed SAP were a little below those reported above for alloyed SAP by the New England Materials Laboratory, but well above those reported for unalloyed SAP in the U.S.A. and Europe. At high temperatures, properties of the U.S.S.R. SAP alloys were comparable to those for the high oxide content SAP alloys reported in the literature.

Discussion and Recommendations

Until about 3 years ago, the level of support for dispersion strengthened alloy systems was extremely small. Support had been available over a 10-year period for minor alloy development programs based almost exclusively on pure metal matrices. Methods for achieving dispersions found a favorable reception, but the studies were often too shallow or the program was dropped before useful results could be obtained.

Support for material processing studies is hardly worth comment. The role of cold work, the nature of the interface between dispersoid and matrix, recovery and recrystallization behavior, and deformation and fracture mechanisms were also largely neglected. In general, forming, shaping, joining, and reworking operations saw little activity and, except for joining studies, continue to find little support.

Stability of structure in long-time, high-temperature exposure has not been examined. The increased use of alloyed matrices, especially chromium for oxidation resistance, has generated a number of questions and problems. Examination of data on a Co-Cr-ThO₂ alloy (ref. 23), of the data on thoria strengthened stainless steel, and of other thoria dispersion strengthened Ni-Cr alloys shows that whereas there is a significant increase in strength up to about 1800° F, above 1800° or 2000° F there is a more rapid decrease in strength in longer time tests as compared, for example, with that of TD-Ni. This drop in strength at the higher temperatures appears to be associated with structural instability. The presence of fairly large amounts of Cr₂O₃, acting as a contaminant, may be decreasing the stability of ThO₂ or other refractory oxides. It is possible that chromium itself may be reacting with the refractory oxide dispersoid. If the latter case is true, other reactive metals,

such as aluminum, titanium, beryllium, and so forth, used as alloying additions to the matrix may also react with the refractory oxide.

Too few tests have been performed to establish long-time creep rupture properties at elevated temperatures. Fatigue and impact properties are very poorly known. Oxidation and corrosion data in various atmospheres are available in limited amounts.

Mechanical property data which exist for these extremely stable alloys are reported usually in terms of stress for a 100-hour or, infrequently, 1000-hour life; yet the real superiority is most evident in the longer time, higher temperature tests. These oxide dispersed alloys look rather mediocre in low- or high-temperature tension tests; unfortunately, there are very few data beyond several hundred hours of test time.

It is well known that TD-Ni is stronger than Udimet 500 or René 41 at 1800° F and above in creep rupture if the test time is 1000 hours or longer; however, it should be of interest to know that thoria dispersion strengthened stainless steel, or a Co-Cr-ThO₂ alloy (ref. 23), is stronger than René 41 at 1500° F if the test time is about 25 000 hours or longer.

It is also not justifiable to compare alloys such as Udimet 700, Inco 713C, or SM-200 with these early oxide dispersion strengthened alloys. In the former case, there is a background of 25 years of research and technology, coupled with millions of dollars of research and development; in the latter case we are dealing with a foundling.

These dispersed phase alloys represent a new, emerging, developing system. They have not had adequate support at the fundamental or applied level. The improved support condition dates back only 2 or 3 years. In view of the great potential for such alloys, first, to fill the temperature gap 1800° to 2400° F (based on oxidation resistant alloys containing Ni, Co, Fe, Cr, etc.), and, at a later date, to improve alloy performance above 2400° F, a stepped-up level of support is warranted.

Where, basically, are the major gaps in knowledge? Without attempting to prepare an all-inclusive listing, the following represent a number of studies which are of importance:

(1) The stability of oxide dispersed structures, including the role of metallic and nonmetallic impurities. This applies especially to

systems containing active solute elements, such as chromium, aluminum, titanium, and so forth.

(2) The mechanism of strengthening. What is the role of stored energy of deformation? Do dislocations persist after recrystallization?

(3) The role of solid solution alloying of the matrix. Can reactive elements (high free energy of formation of the oxide, for example) be utilized in metal-metal oxide alloys?

(4) The manufacture of metal-metal oxide alloys by powder metallurgy methods. The least expensive and the widest range of alloy compositions are potentially producible by use of fine alloyed powders.

(5) Concentration on oxidation resistant alloy systems. Our knowledge of high-temperature alloys in terms of solid solution strengthening is minute, yet such knowledge should serve as the basis of alloyed metal-metal oxide materials.

(6) An intimate understanding of the role of cold work, intermediate annealing treatments, and cumulative energy storage in terms of dislocation density and patterns, properties, and stability.

(7) Fabrication of finished parts. When should one use high extrusion ratio versus low extrusion ratio plus cold work processing? What is the role of texture (oxide as well as matrix) on properties?

(8) Do intermetallic dispersion strengthened alloys offer advantages over oxide dispersed alloys?

(9) What are the long-time, high-temperature creep properties (tension, compression, and torsion)? What is the fatigue performance, and how do structural variables affect such performance? What are the thermal fatigue and thermal shock characteristics? What are the impact properties over a wide temperature range?

(10) What improvements can be incorporated into joining methods to improve utility? Is cladding (compared with U.S.S.R. experience with SAP alloys) a potential aid in joining? In brazing or diffusion bonding, what type of diffusion is likely to damage the structure? Does texture make all joining more difficult? How useful are spot welding, seam welding, and butt and flash welding?

These, then, are areas which clearly require probing. The answers are not now available. We believe that the answers should be sought in a more aggressive, well-coordinated support program.

Appendix

COMMENTS BY MEMBERS OF NASA RESEARCH ADVISORY COMMITTEE ON MATERIALS AND MEMBERS OF NASA RESEARCH STAFF

THE FAILURE OF THE AEROSPACE INDUSTRY to develop applications for SAP is largely due to the inherent low mechanical property level exhibited by this material at room temperature. In figures A-1 and A-2, the tensile properties are compared for two dispersion

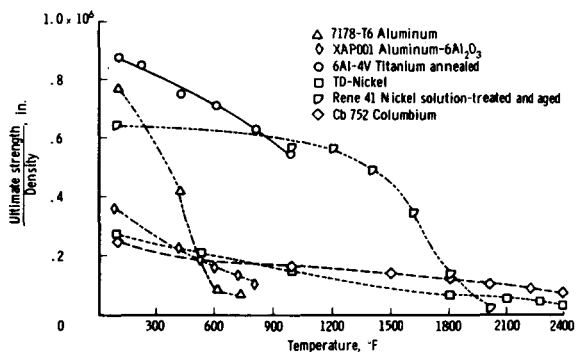


FIGURE A-1.—Yield strength-density ratio plotted against temperature.

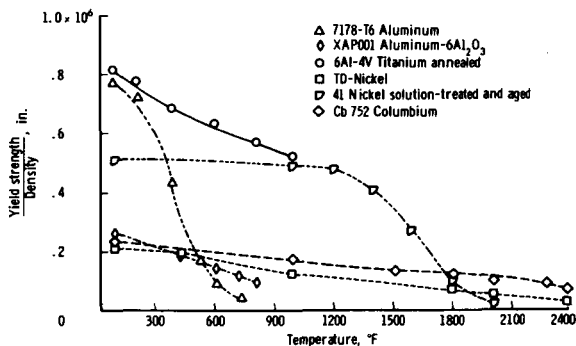


FIGURE A-2.—Ultimate strength-density ratio plotted against temperature.

strengthened and four conventional alloys, all on a density-compensated basis. It can be seen that the conventional aluminum alloy (7178-T6) has an advantage of more than 2:1 over XAP001, a SAP-type material, at room temperature. It is true that SAP offers higher short-time mechanical properties from about 600° to 1000° F, and that, unlike conventional alloys, its strength is stable for long time exposures at temperatures above 350° F. However, titanium and its alloys, as also shown in figures A-1' and A-2, clearly demonstrate their superior efficiency in this temperature range. The SAP alloys are structurally less efficient than competitive materials, at least for our applications, over their entire temperature range. If we now consider TD-Ni and competitive materials, we find that, at temperatures up to 1800° F for airframe applications, René 41 is a more efficient structural material, is significantly less expensive, and may be fabricated and joined using conventional techniques with which most fabricators are familiar. At temperatures above about 1800° F, TD-Ni is more efficient than the conventional superalloys, but in this temperature range it competes with refractory alloys. The density compensated ultimate tensile strength and yield strength of TD-Ni are compared with Cb-752, a typical moderate strength columbium alloy and René 41. It is apparent from this comparison that one would never select TD-Ni based upon short time strength alone. The substantially better oxidation resistance of TD-Ni compared with the refractory alloys is the sole basis for its consideration for applications in the 1800° to 2400° F temperature range. However, the oxidation resistance of TD-Ni is not sufficient in this temperature range to allow use of light gage sheet (0.020-inch thickness or less) for applications requiring a useful part life as short as 50 hours without use of an oxidation protective coating.

Since TD-Ni must be protectively coated, cannot be joined by conventional metallurgical techniques, offers no particular fabrication advantages, and is less efficient structurally than comparative columbium base alloys, its primary advantage is lower cost (\$30 per lb as opposed to \$80 per lb for sheet). However, for most of the vehicles for which TD-Ni might be considered, the \$50-per-pound cost savings resulting from use of TD-Ni cannot compensate for the added vehicle weight.

Obviously, additional development of dispersion strengthened materials is required. The three primary avenues along which progress must be made to make these materials really useful for structural airframe applications are:

- (1) Improved strength
- (2) Improved oxidation resistance

- (3) Development of reliable and practical metallurgical joining techniques.

—HOWARD J. SIEGEL, *McDonnell Company*

I BELIEVE that progress has been relatively slow because a widely recognized need of sufficient importance to attract substantial Government support has not coexisted with availability of a dispersion strengthened alloy with sufficiently promising properties. Currently the situation is more favorable. The recognized need for higher operating temperatures in jet engines of the proposed supersonic transport has focused attention on dispersion strengthened nickel- and cobalt-base alloys. TD-nickel is now available and has sufficiently promising properties to foster effort aimed at overcoming its deficiencies. The need to operate in air for long times at temperatures close to the melting points of superalloys is real and apparent. It also appears that alternate materials such as coated refractory metals are very unlikely to achieve the reliability requirements of this application. Thus I believe that the time is ripe for focusing a significant effort on dispersion strengthened, oxidation resistant materials.—

ROBERT W. HALL, *Lewis Research Center, NASA*

IN MY OPINION there are two reasons why we have not made the most rapid possible progress in utilizing dispersion strengthened alloys:

- (1) The effort has been somewhat misdirected.

- (2) The effort has been too small in relation to what is required to make rapid progress.

In support of my view that the effort has been somewhat misdirected, I offer the following more detailed arguments:

- (1) The effort has not been concentrated in materials where the need would justify the development.

- (2) The investigators who worked in the area where need was great did not focus their work on the important question.

In regard to the first argument, significant effort has been directed toward the refractory metals where conventional melted or powder metallurgy alloys seem more than able to meet the needs. Even if an outstanding material could be produced, it would not be needed.

Even where the work was in an area of great need, namely in superalloys, I suggest that early investigators were not framing the

proper questions for their research. It seems to me our model system since metallurgists became excited over dispersion systems has been SAP. Particular features of this system are:

- (1) A very stable dispersed particle
- (2) A very fine particle spacing (and size)
- (3) The strength versus temperature curve exhibited an unusually flat slope showing a strength advantage, but only at temperatures *above* those at which the conventional alloys were unstable.
- (4) The microstructure also exhibited unusual stability to almost the melting point.
- (5) Cold work made a very important contribution to strengthening (this may not have been recognized early).
- (6) A trade-off in ductility was indicated—high strengths tended to be achieved with higher volume additions but at a sacrifice in room temperature ductility.

Yet it is my impression that many of the researchers working on dispersion strengthened superalloys have not correctly approached the problem.

- (1) They measured strengths only at temperatures of 1500° F or so—at the temperatures where the more sophisticated alloys were at their best. The most that could be said for the dispersion strengthened materials at this temperature was that they were a little better than the matrix pure metal. Properties at 1800° F and 2000° F were not measured.

- (2) Almost none of the products produced had particle sizes or spacing anything like SAP, yet many expensive billets and extrusions were produced and extensive rupture tests were run.

- (3) Simple metallurgical tests (stability anneals) could have been run to indicate whether the microstructures were stable at very high temperatures, but instead, the investigators too often focused their attention on expensive production of material for rupture tests (on materials that could have been proved unsatisfactory in simple annealing tests).

- (4) I also believe that until recent years we may have failed to recognize the great detriment that impurities can have on stability and properties (particularly in nickel-base systems) and the importance of controlled cold work.

In regard to my comment that the effort has been too small, I think that everyone recognizes that the development of any process or concept to "bring in" a new class of materials is extremely expensive. The dispersion strengthened systems are among the more difficult and thus among the more expensive. The money invested by the government to achieve *needed* materials, however, is a small frac-

tion of the money invested in other new material areas such as titanium or fibers. (I would guess, too, that the investment in the TD products is more than twice that in all other dispersion strengthened systems.)

Now that I have presented arguments and criticisms of our procedures that have led to our slow progress, I would like to argue that in spite of our "low effort and misdirection," progress has actually been quite good.

I think that Grant et al. produced a quite sophisticated dispersion material in their copper systems, and Battelle Memorial Institute researchers have shown that thoria dispersions can lower the ductile-brittle transition temperature in tungsten. Most important are dispersion strengthened nickel products by Du Pont and Sherritt Gordon. It is clear that TD-nickel and/or TD-nickel-chromium will be used for stator vanes of prototype or production engines very soon; that is the goal that was sought.

Let us be sure that development and research continue. We need:

- (1) Materials of higher strength at low temperatures (comparable to conventional superalloys down to 1350° F) to permit these materials to be used in rotating buckets.

- (2) Materials of higher strength at all temperature levels to permit higher service temperatures than dispersion strengthened nickel or dispersion strengthened nickel-chromium.

Undoubtedly this will involve more studies of alloy matrices, cold work, perhaps in combination with precipitate strengthening.

Surely there will be other suitable processes than those of Du Pont and Sherritt Gordon. In many cases the process and the composition will need to be tied together. Change in composition will require a change in process. (Some processes will not have this limitation.) Before investing large sums, I urge that we screen the processes and compositions by simple laboratory tests on small samples to see if we have:

- (1) Fine spacing and particle sizes.

- (2) Stability of the microstructure after very high temperature anneals

- (3) Whether the structure will retain cold work at proposed use conditions (if possible).

If the process and material pass this screening, we can then proceed to scale up to investigate the effect of degree of cold work and particle spacing (and size) on strength and ductility.

I also believe a most difficult problem, once we are a little farther along with these materials, will be the trade-off between strength

and ductility. Some of these systems will fail because needed ductility is lost when we have arrived at the target strength levels.—
G. M. AULT, *Lewis Research Center, NASA*

BEFORE AN ATTEMPT IS MADE TO ANSWER THE QUESTION, "Why have oxide dispersion strengthened systems received so little attention and support?" let me dismiss as rationalizations the reasons frequently cited for the lack of progress. Some of these are:

- (1) The field is most difficult to work in
- (2) The time between the starting of the production of a product to the time required to obtain a specimen is long, sometimes on the order of several months
- (3) The materials are most difficult to fabricate successfully.

Let me at this point review some of the pertinent milestones in the dispersion strengthened materials field. Rhines, in 1942 and 1947, described internal oxidation and its capability of retarding recrystallization. Then in 1947 Meijering and Druyvesteyn (ref. 3) produced what could be considered dispersion strengthened materials by internal oxidation. They even demonstrated that annealing treatments did relatively little to reduce the strength of the cold-drawn materials. Such results were an indication of the stabilizing characteristics of oxides on metallic structures. In neither of these cases was there any recorded effort to exploit the potentialities of the results. The authors were academically inclined and "internal oxide oriented."

Next came Irmann, and some of his early papers (in the 1949–1952 period) had a fantastic amount of information. He showed, to some degree at least, the importance of microstructural parameters and even in some cases the effects of cold work upon properties. From his work it could be deduced that his as-extruded material was "stuffed" with stored energy. Cremens, Bryan, and Grant, working with aluminum, corroborated the fact that cold work was important to dispersion strengthened aluminum materials and indicated by their data at least that as-extruded SAP had a large quantity of stored energy. Later Preston and Grant, in working with internally oxidized copper systems, showed some properties for copper-alumina that had unusual implications. Some of the materials had SAP-analog strength for long-time stress-rupture conditions. These authors also stated that "plastic working after the formation of the dispersion is an essential feature of the hardening mechanism in these alloys."

There was an implication in the results of Preston and Grant

which may not have been so obvious to the reader; namely, that internally oxidized products were much stronger than mechanically mixed products. This further suggested that the combined scavenging action and subsequent oxide formation reaction was very beneficial to such products and indirectly suggested that a similar advantage might be obtained by alloying additions.

Some of us found out the hard way that impurities were a major problem. This problem plagued one investigator after another and essentially prevented the production of good dispersion strengthened materials, particularly dispersion strengthened superalloy types of materials containing oxidation resistant elements. One operation which essentially prevented the production of a good product was the cleaning of the starting powders. Another was the consolidation operation itself which often produced agglomerates of the dispersoid added. What was not fully appreciated was that, whether a researcher wanted to develop a high-strength product, or whether a fundamentalist wanted to study a product, first a method to produce something worth working on had to be developed.

Much more can be said about the happenings of the past, but it was only with the appearance of TD-nickel that there was any assurance that a good potentially commercial product could be produced. This is not to deny that the work that had been done in copper had commercial implications, but most of the people interested in dispersion strengthened materials wanted materials for use in the temperature range of 1800° F to over 4000° F.

There have been two extremes of effort in the area of dispersion strengthened materials. One was the effort of the fundamentalist who has studied the effects of dislocation pileups, and so forth, on materials that he himself has made or obtained. These products contained varying percents of impurities. Unfortunately, far too much emphasis was placed on high and low temperature tensile phenomena rather than on creep-rupture (where SAP had an obvious potential advantage) particularly at long times and very high temperatures. The other efforts that abounded included developmental work. Here every novel trick of the trade to produce a dispersion strengthened product has been tried. Some investigators attempted to apply both the fundamental and developmental concepts to produce products.

Inhibitions seemed to plague investigators differently throughout the years. At least some of those who followed the pioneer investigators referenced the earlier works but seemed not to take seriously the concepts they contained; for example, the concept that "stored energy" or mechanical processing is important to produce good dispersion strengthened materials. Others discounted the practical dif-

ferences between lower melting systems and higher melting systems. Still others felt that to understand dispersion strengthened products, a pure metal should be used. The stored energy concept should have suggested that, if a matrix must be cold-worked, one should select an alloy matrix that retained cold work rather than a pure matrix. In actuality, an alloy such as nickel with 2 percent aluminum is in many senses more analogous to aluminum than is pure nickel. Another inhibition, largely associated with the fundamental powder metallurgist, was an obsession with holes and pores. The fact that holes and pores can be closed by extrusion and forging practices did not deter many an investigator from fantastic efforts to achieve high densities in starting products. Finally, investigators seemed to hesitate to roll rather than extrude materials. Those who produced some of the best products have used rolling to good advantage.

Where do we stand today? Possibly unusually good materials may soon be made by several methods. Some already have been made by such methods as that for producing TD-Ni and the Sherritt Gordon dispersion strengthened nickel. Internally oxidized products produced by industry and the MIT group have also been most strong and stable.

Today there is no question in my mind that we shall soon see breakthroughs in the form of strong commercially applied dispersion strengthened single phase and alloy materials produced by a number of different methods.—J. W. WEETON, *Lewis Research Center, NASA*

WITH RESPECT TO THE HISTORY OF DISPERSION STRENGTHENING, I would agree that dispersion strengthening probably came of age around 1955 or 1956. For example, there was a Gordon Research Conference about this time which was an effective stimulant to widespread interest. In evaluating the rate of progress one should consider three types of knowledge or work:

- (1) The relationships between structure and properties. By 1955 it was clear that a *stable* dispersoid, inert with respect to the matrix, could provide properties which were at least interesting and hopefully of practical benefit. Although much more has been learned since then, our knowledge of structure-property relationships is still far from mature. Currently, there is a renaissance of such studies with considerable activity and some healthy controversy. It is hoped that this will provide new insight into the types of preparation conditions and eventual structures needed for useful properties.

(2) The ability to synthesize desired structures. During the late 50's many of us felt that this was a pacing factor; that a variety of approaches and techniques for synthesizing different dispersion strengthened structures would be necessary. I think the evolution of the processing method leading to TD-Nickel was progress in this direction, and that this major step forward provided stimulus to the entire field.

(3) The application of knowledge derived from (1) and (2) above to yield useful new materials, first in the laboratory and then in production.

Recognizing the general resurgence of interest in and support for work in categories (1) and (2), the strategy for spending our own "applied" resources has been to provide some additional stimulus to (2) and to concentrate on (3) in an attempt to capitalize on the knowledge which is, or should be, emerging. Thus, work in both nickel and cobalt systems is now being supported, and some of this is very promising. There is also support of some work on other alloy systems, and in-house work under Drs. Gegel and Lynch.

Looking toward the future we would certainly agree with the strategy of emphasizing oxidation resistant systems. Metal or ceramic matrix composites have also been discussed, with talk about an oxidation barrier rather than a thermal barrier. There are many special cases where some environmental characteristic other than oxidation is important, but the "sea of air" we fly in is always first on our list. Furthermore, some of our current manufacturing technology work does represent a pilot operation on oxidation resistant systems, and we certainly plan to elevate other possibilities to pilot plant or production scale status, when and if they show sufficient promise to warrant it.—COL. LEE R. STANDIFER, *Wright-Patterson AFB*

LANGLEY'S INTEREST IN OXIDE STRENGTHENED MATERIALS developed in the early 1960's. When a commercial product, thoriated nickel, became available, an experimental investigation was initiated to study this material. The study covered mechanical and physical properties, fabrication including machining and joining, oxidation characteristics, and protective coatings. The results of this work are given in NASA TN D-1944 entitled, "An Investigation of a New Nickel Alloy Strengthened by Dispersed Thoria," by Charles R. Manning, Jr., Dick M. Royster, and David N. Braski. Further details of this study with emphasis on diffusion bonding were presented at the eighth meeting of the Refractory Composites Working Group, January

14-16, 1964, Fort Worth, Texas, in a paper entitled, "A Preliminary Study of the Solid-State Bonding of Thoria Dispersion Strengthened Nickel," by Thomas T. Bales and Charles R. Manning, Jr. On the basis of experience obtained from these studies the following comments are offered:

(1) Utilization of oxide dispersion strengthened materials is being handicapped by poor availability and relatively high cost.

(2) The strength of oxide dispersion strengthened nickel, although superior to current superalloys, is still very low.

(3) Considerably more attention should be devoted to fabrication problems associated with usage. Solid-state or diffusion bonding may prove feasible in some applications; however, this method for joining is in its infancy.

(4) Oxidation resistance, although not too poor, should be improved considerably to be competitive with the better grades of nickel- or cobalt-base alloys.

It is believed that these four points are major reasons for the slow progress in utilization of oxide dispersion strengthened materials. We have no comments to offer relative to the early development history of such materials.

Langley is currently sponsoring no work out-of-house in oxide dispersion strengthened alloys.—ELDON E. MATHAUSER, *Langley Research Center, NASA*

THE WORK OF IRMANN AND VON ZEERLEDER excited immediate interest when it was brought to the attention of the Government sponsoring agencies by Dix and his coworkers at Alcoa. The number of research projects supported in the early years in an attempt to exploit the SAP concept was very substantial. Yet many of them were so inconclusive or nonproductive that they were not reported in the permanent technical literature.

The results of much of this work followed a set pattern: the first experiments produced a material which was stronger and more resistant to high temperature softening than the pure matrix but which was less enticing when compared with the good commercial alloys. Two or three years of additional work then produced no further improvements.

Why was this so? Mainly because the work concentrated on getting useful commercial alloys, before the necessary body of basic science and supporting technology was established. It could reasonably be claimed that the field was oversupported. Much effort was wasted in

trying to dispersion strengthen metals poorly suited to this technique while paying inadequate attention to the enormous difficulties. There were efforts devoted to titanium, niobium, molybdenum, and practically every other glamorous metal. The need for high-quality fine powders encouraged numerous attempts to produce them by any technique which appealed to the imagination, again without adequate recognition of the technological difficulties.

In the low-temperature systems the situation was better. The MIT group had substantial success with copper-base systems. Lenel, at Rensselaer Polytechnic Institute, worked profitably with lead and, I believe, zinc. Both of these teams also contributed the badly needed basic knowledge on the effect of particle size and spacing, on annealing behavior, and on structure as revealed by electron microscopy. I think the success with low-temperature alloys was due to two factors:

- (1) The competition was not so keen. Commercial alloys in these systems had not been optimized for high-temperature stability to anything like the same extent as, say, the superalloys.

- (2) The problems were not so severe. Atomic mobility is much less a problem below 1000° F than above 1800° F.

During this period the aircraft industry took a hard look at dispersion strengthened aluminum but rejected it for most applications because of three deficiencies:

- (1) The room temperature strength was inferior to that of precipitation hardened alloys.

- (2) Attempts at fusion welding produced porosity and agglomeration of dispersoid in the weld area.

- (3) Ductility decreased with temperature and was marginal at the desired service temperatures.

A fourth deficiency precluded serious consideration of the nickel-base dispersion strengthened alloys—their inadequate oxidation resistance at high temperature.

Starting about 1962, the power plant requirement for materials capable of long-time service just above 1800° F became acute. At the same time several factors combined to lift dispersion strengthening technology out of the depressed state into which it had descended:

- (1) The new chemical processes allowed production of nickel matrix alloys at acceptable cost in usable quantity.

- (2) The more basic techniques, including sophisticated X-ray and transmission microscopy, related thermomechanical history to substructure and to matrix-dispersoid interactions. For example, the role of "stored energy" which had been noted empirically by several of the early investigators began to fall into place.

(3) Better controlled experiments produced the beginning of understanding of factors affecting comminution and agglomeration.

(4) Alloy matrix materials, including oxidation resistant alloys, slowly began to make their appearance.

(5) Solid-state bonding techniques helped with the joining problem.

What about the future? I consider it quite promising if we learn from the mistakes of the past. We are dealing with what is likely to be the most complex stabilizing mechanism the materials engineer has ever had placed at his disposal. Learning to control it will not be a short-time effort, nor will empirical research stand more than a minimal chance of success.—JOSEPH MALTZ, *NASA Headquarters*

References

1. ZEERLEDER, A. V.: Über Sintern von Aluminum Legierungen. *Zeitschrift für Metallkunde*, vol. 41, 1950, pp. 228–231.
2. RHINES, F. N.: Metallographic Study of Internal Oxidation in Alpha Solid Solutions of Copper. *Trans. Am. Inst. of Mining and Metall. Eng.*, vol. 137, 1940, pp. 246–290.
3. MEIJERING, J. L.; and DRUYVESTYEN, M. J.: Hardening of Metals by Internal Oxidation, pt. 2; *Phillips Res. Rep.*, vol. 2, 1947, pp. 260–280.
4. MARTIN, J. W.; and SMITH, G. C.: Preliminary Note on Creep Properties of Internally Oxidized Copper Alloys. *J. Inst. Metals*, vol. 83, May 1955, pp. 417–420.
5. IRMANN, R.: Gesintertes Aluminium mit hoher Warmfestigkeit. *Aluminium*, vol. 27, no. 2, Oct. 1951.
6. IRMANN, R.: L'Aluminium Fritté à Haute Résistance à La Chaleur. *Revue de L'Aluminium*, vol. 28, no. 180, Sept. 1951, pp. 316–331.
7. IRMANN, R.: Heat Resistant Sintered Aluminium. *The Engineers' Digest*, vol. 13, no. 1, Jan. 1952, pp. 9–12.
8. LYLE, J. P.: Excellent Products of Aluminum Powder Metallurgy. *Metal Progress*, vol. 62, no. 6, Dec. 1952, pp. 109–112.
9. GREGORY, E.; and GRANT, N. J.: Aluminum Powder Products. *The Iron Age*, vol. 170, no. 26, Dec. 25, 1952, p. 69.
10. GREGORY, E.; and GRANT, N. J.: High Temperature Strength of Wrought Aluminum Powder Products. *Trans. AIME*, vol. 200, 1954, p. 247.
11. LENEL, F. V.; BACKENSTO, A. B.; and ROSE, M. V.: Properties of Aluminum Powders and of Extrusions. *Trans. Met. Soc., AIME*, vol. 209, 1957, p. 124.

12. LENEL, F. V.; et al.: Metallography of Aluminum Powder Extrusions. WADC-TR-56-170, 1956.
13. GRANT, N. J.; and PRESTON, O.: Dispersed Hard Particle Strengthening of Metals. Trans. Met. Soc., AIME, vol. 209, 1957, p. 349.
14. ZWILSKY, K. M.; and GRANT, N. J.: Copper Silica and Copper-Alumina Alloys of High Temperature Interest. Trans. Met. Soc., AIME, vol. 209, 1957, p. 1197.
15. BRUCKART, W. L.; CRAIGHEAD, C. M.; and JAFFEE, R. I.: Investigation of Molybdenum-Base Alloys Made by Powder Metallurgy Techniques. WADC Tech. Rep. 54-398, Jan. 1955.
16. CREMENS, W. S.; and GRANT, N. J.: Preparation and High Temperature Properties of Nickel- Al_2O_3 Alloys. Proc. ASTM, vol. 58, 1958, p. 714.
17. ZWILSKY, K. M.; and GRANT, N. J.: Dispersion Strengthening in the Cu- Al_2O_3 System. Trans. Met. Soc., AIME, vol. 221, 1961, p. 371.
18. PRESTON, O.; and GRANT, N. J.: Dispersion Strengthening of Cu by Internal Oxidation. Trans. Met. Soc., AIME, vol. 221, 1961, p. 164.
19. TRACEY, V. A.; and WORN, D. K.: Some Observations on Cold-Drawing and Annealing Behavior of Nickel Containing Dispersed Phase of Thoria. Powder Metall., no. 10, 1962, pp. 34-48.
20. RISÖ STAFF: Metallurgy Section, Annual Progress Report for Period Ending March 31, 1964. Danish Atomic Energy Commission Res. Est. (RISÖ), Risö Report No. 90, Aug. 1964.
21. ANON.: Heavy Water Organic Cooled Reactor; SAP Handbook. AI-CE-Memo-24. U.S. Atomic Energy Commission, Mar. 23, 1966.
22. FRIDLYANDER, I. N., ed.: Aluminum Alloys—A Compilation. Second ed., Oborongiz (Moscow), 1963.
23. BUFFERD, A. S.; and GRANT, N. J.: Oxide Dispersion Strengthening of Cobalt-Base Alloys. Journées Internationales des Applications du Cobalt (Brussels), June 9-11, 1964, p. 251.